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ROOM-TEMPERATURE CURABLE COMPOSITION
[Shitsuon Kokasei Soseibutsu]

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ROOM-TEMPERATURE CURABLE COMPOSITION

(1) A room-temperature curable composition that contains a
 ether compound, said polyether compound being composed of

$$\begin{array}{c}
 \text{R}^1, \quad \text{R}^2, \quad \text{R}^1 \\
 | \quad | \quad | \\
 \text{X}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2\text{CH}-\text{Z} \\
 | \\
 \text{X}_2- \\
 | \\
 \text{Y}-\text{Z}-\text{CHCH}_2-\text{Si}-\text{O}-\text{Si}-\text{X}_2 \\
 | \quad | \quad | \\
 \text{R}^1, \quad \text{R}^2, \quad \text{R}^1
 \end{array}
 \quad (I)$$

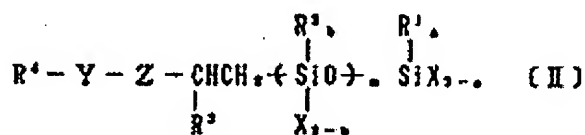
X represents a hydrolyzable functional group,

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Y represents a polyoxyalkylene polymer chain, and

Z represents any group selected from a group consisting of -R-, -ROR-, -ROC(=O)-, -RC(=O)-, -RNHC(=O)-, and -C(=O)- (wherein Rs represent C₁₋₂₀ divalent hydrocarbon groups of the same kind or different kinds), said polyether having hydrolyzable silicon functional groups at both terminals of the molecular chain, and of

(B) 90 to 10 % by weight of a polyether represented by General Formula II below:



wherein

a, b, m, and R¹ through R³ have the same meanings as defined in the foregoing, and

R⁴ represents a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms, said polyether /358
having a hydrolyzable silicon functional group at one terminal of the molecular chain,
and that contains (C) a curing catalyst.

(2) A cured product that is obtained by curing the composition stated in Claim 1.

3. Detailed Description of the Invention

[Field of Industrial Application]

The present invention pertains to a room-temperature curable composition that is comprised of polyether having hydrolyzable silicon functional groups.

[Prior Art]

Polyethers that have hydrolyzable silicon functional groups have a characteristic of curing when exposed to the moisture in the atmosphere and becoming rubber-like substances, and they are used for such applications as adhesives, sealing agents, and the like.

This type of polyether is generally mixed with plasticizers, fillers, and so forth and put to various applications in the form of compositions. For example, in the case of using it as a construction-use sealant, it is required to have a low modulus and high elongation rate; therefore, it has been a common practice to mix this polyether with a plasticizer, such as non-functional polyether, etc., and use it as a composition.

[Problems that the Invention Intends to Solve]

However, in order to obtain cured products that have a low modulus and high elongation rate from the aforesaid type of polyether, it is necessary to blend a plasticizer in a large quantity.

The cured products that are obtained from a polyether composition in which a plasticizer is blended in a large quantity have a problem

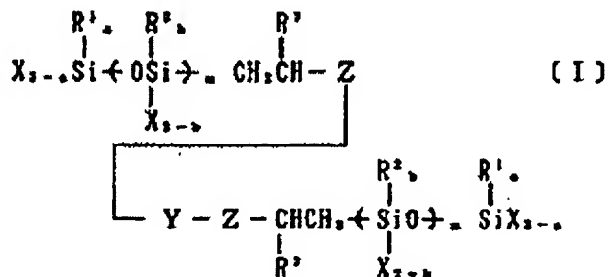
in that the plasticizer bleeds out to the surface of the cured products over time and causes such problems as a tacky surface and so forth. There is another problem in that, because the plasticizer bleeds out to the surface of the cured products, the physical properties, such as hardness, elongation, and the like of the cured products change.

Accordingly, the present invention intends to provide a polyether composition that can effectively solve the problem of bleeding of a plasticizer to the surface of cured products and also makes it possible to obtain cured products having a low modulus and high elongation rate.

[Means for Solving the Problems]

The present invention provides a room-temperature curable composition that contains a polyether compound, said polyether compound being composed of

(A) 10 to 90 % by weight of a polyester represented by General Formula I below:



wherein

a and b each represent an integer of 0 to 2,

m represents an integer of 0 to 18,

R¹ represents a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms,

R² represents a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms or an organosiloxy group,

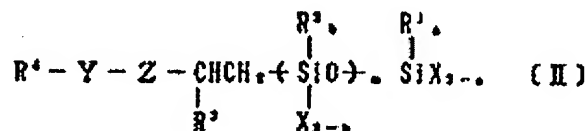
R³ represents a hydrogen atom or a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms,

X represents a hydrolyzable functional group,

Y represents a polyoxyalkylene polymer chain, and

Z represents any group selected from a group consisting of -R-, -ROR-, -ROC(=O)-, -RC(=O)-, -RNHC(=O)-, and -C(=O)- (wherein Rs represent C₁₋₂₀ divalent hydrocarbon groups of the same kind or different kinds), said polyether having hydrolyzable silicon functional groups at both terminals of the molecular chain, and of

(B) 90 to 10 % by weight of a polyether represented by General Formula II below:



wherein

a, b, m, and R¹ through R³ have the same meanings as defined in the foregoing, and

R⁴ represents a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms, said polyether having a

terminal-modified polyether having hydrolyzable silicon functional groups at both terminals of the polyether polymer chain.

In General Formula I, a and b are integers of 0 to 2, and m is an integer of 0 to 18. As is evident from the value of this a, the silicon atoms at both terminals of the molecular chain must have group X bound to them, while it is not essential for group R¹ to bind to said silicon atoms.

Group X is a hydrolyzable group, and some examples of this hydrolyzable group include alkoxy groups, such as a methoxy group, ethoxy group, propoxy group, butoxy group, methoxy ethoxy group, ethoxy ethoxy group, etc.; acyloxy groups, such as an acetoxy group, propionoxy group, butyloxy group, etc.; alkenyloxy groups, such as a propenyloxy group, isobutenyloxy group, etc.; iminoxy groups, such as a dimethyl ketoxime group, diethyl ketoxime group, methylethyl ketoxime group, cyclopentanoxime group, cyclohexanoxime group, etc.; amino groups, such as an amino group, N-methylamino group, N-ethylamino group, N-propylamino group, N-butylamino group, N,N-dimethylamino group, N,N-diethylamino group, etc.; amide groups, such as an N-methylacetamide group, N-ethylacetamide group, N-methylpropionamide group, etc.; and aminoxy groups, such as an N,N-dimethylaminoxy group, N-methyl-N-ethylaminoxy group, N,N-diethylaminoxy group, etc. Owing to the presence of this type of group, this Component A polyether exhibits a condensation curing property.

Group R¹ is a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, some examples of which include alkyl groups, such as a methyl group, ethyl group, propyl group, butyl group, octyl group, etc.; cycloalkyl groups, such as a cyclopentyl group, cyclohexyl group, cyclobutyl group, etc.; aryl groups, such as a phenyl group, tolyl group, xylyl group, naphthyl group, etc.; aralkyl groups, such as a benzyl group, phenylethyl group, phenylpropyl group, etc.; and such groups as a chloromethyl group, 3,3,3-trifluoropropyl group, and the like, which are obtained by substituting halogen atoms for some or all of the hydrogen atoms that bond with these hydrocarbon groups.

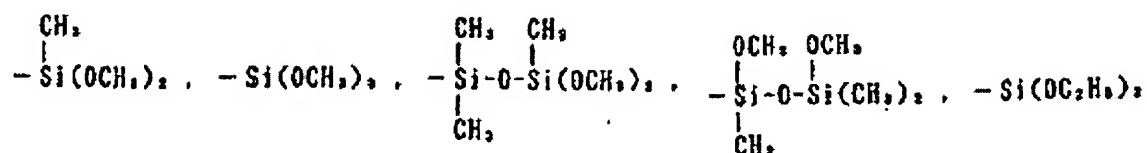
Group R² is a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, or an organosiloxy group. Examples of such a monovalent hydrocarbon group include the groups that are presented as examples of the aforesaid R¹. Examples of the organosiloxy group include a trimethylsiloxy group and the like.

In the present invention, especially suitable examples of the hydrolyzable silicon functional groups at the molecular terminals that are constituted from the aforesaid groups, that is,



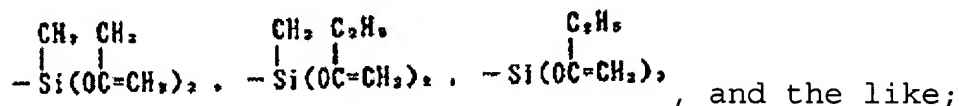
include: alkoxysilyl groups, such as

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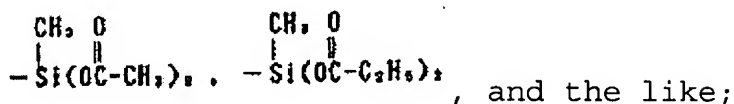


and the like;

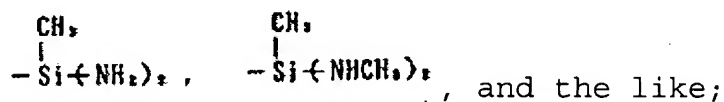
alkenyloxysilyl groups, such as



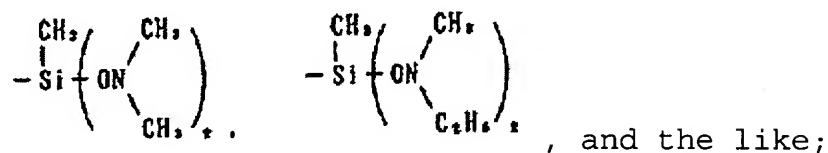
acyloxysilyl groups, such as



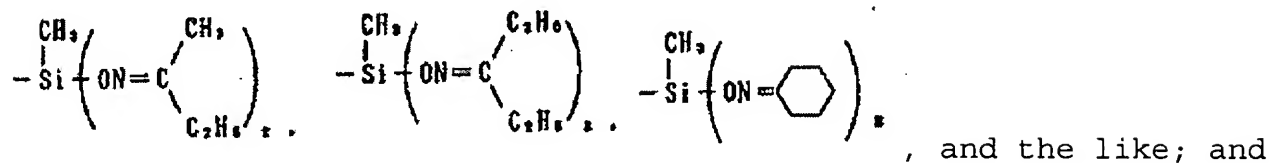
aminosilyl groups, such as



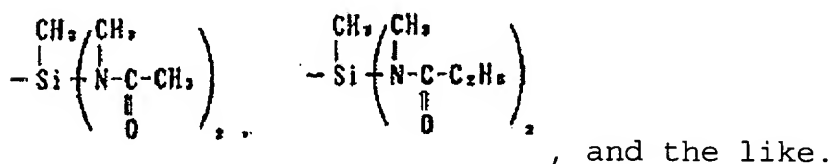
aminoxysilyl groups, such as



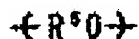
iminoxysilyl groups, such as



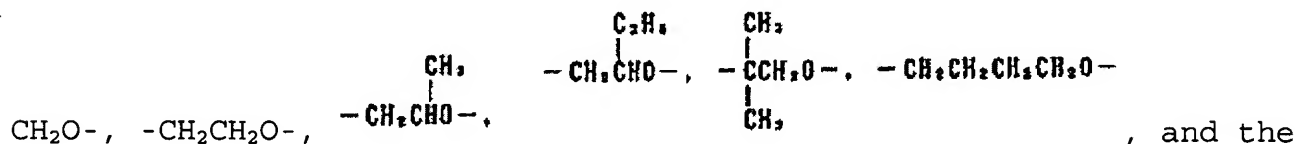
amidosilyl groups, such as



In the aforesaid General Formula I, Y represents a polyoxyalkylene polymer chain, and it constitutes the main chain of Component A, that is, a polyether whose terminals are both modified. More specifically, said Y is a polyether polymer chain that is composed of a repeating unit represented by the following formula:



(wherein R⁵ is a divalent hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms.) As this repeating unit, -



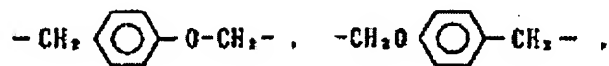
, and the like are especially suitable, and these may be used singly or as a mixture of two or more kinds. Among them, -(CH_[illegible])CHCH₂O- is ideal. The molecular weight of the polyether corresponding to this Group Y is preferably in the range of from 300 to 15,000, better yet, in the range of from 3,000 to 12,000.

Z is a group selected from a group consisting of -R-, -ROR-, -ROC(=O)-, -RC(=O)-, -RNHC(=O)-, and -C(=O)- (wherein Rs represent divalent hydrocarbon groups having 1 to 20 carbon atoms, preferably 1 to 12 carbon atoms.) Concrete examples of group R here include alkylene groups, such as a methylene group, ethylene group, propylene group, butylene group, etc., and aralkylene groups, such as



, and the like. Concrete examples of group -

ROR- include $-\text{CH}_2\text{OCH}_2-$, $-\text{CH}_2\text{CH}_2\text{OCH}_2-$,



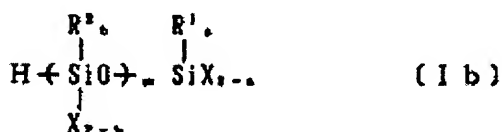
and the like. For the present invention, a methylene group is the most suitable group Z.

In the aforesaid General Formula I, R^3 is a hydrogen atom or, like the aforesaid R^1 , a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms. Concrete examples of this monovalent hydrocarbon groups include alkyl groups, such as a methyl group, ethyl group, propyl group, butyl group, octyl group, etc.; cycloalkyl groups, such as a cyclopentyl group, cyclohexyl group, cyclobutyl group, etc.; aryl groups, such as a phenyl group, tolyl group, xylyl group, naphthyl group, etc.; aralkyl groups, such as a benzyl group, phenylethyl group, phenylpropyl group, etc.; and such groups as a chloromethyl group, 3,3,3-trifluoropropyl group, and the /361 like, which are obtained by substituting halogen atoms for some or all of the hydrogen atoms that bond with these hydrocarbon groups. Among these, a hydrogen atom and a methyl group are ideal, of which a hydrogen atom is especially suitable.

The polyether represented by the aforesaid General Formula I, both terminals of which are modified, can be prepared easily by an addition reaction of a polyether (whose main chain is comprised of the aforesaid repeating unit) having an olefin group represented by the following formula Ia at both ends of the molecular chain:



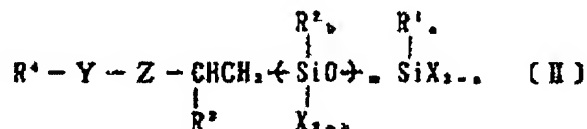
(wherein Z and R² have the same meanings as defined in the foregoing) and a silicon hydride compound represented by the following formula Ib:



(wherein a, b, m, R¹, R², and X have the same meanings as defined in the foregoing) in the presence of a known hydrosilylation catalyst, such as chloroplatinic acid, etc., at a temperature ranging from room temperature to 200 °C.

Component B

The polyether used as Component B in the present invention is a polyether that is represented by the aforesaid General Formula II, that is:



(wherein a, b, m, R¹, R², [sic] Y, and Z have the same meanings as defined before.) As is evident from said General Formula II, this

polyether has a hydrolyzable silicon functional group at one terminal of the molecular chain.

In the present invention, the aforesaid one-terminal-modified polyether is used in combination with the aforesaid both-terminal-modified polyether, and this combined use makes it possible to form a cured product having a low modulus and high elongation rate without the incorporation of a plasticizer. As a result, it becomes possible to effectively avoid the bleeding of a plasticizer (hereinafter simply referred to as "oil bleeding") from the surface of said cured product.

In the aforesaid General Formula II, a, b, m, R^1 through R^3 , Y, and Z have the same meanings as defined in reference to General Formula I, and, as concrete examples of each group, the same examples can be presented.

R^4 represents a substituted or non-substituted monovalent hydrocarbon group having 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, and concrete examples of it include those that are presented as examples of the aforesaid R^3 .

This Component B, one-terminal-modified polyether, is incorporated into a cured product and immobilized by means of the hydrolyzable silicon functional group that is formed at one terminal.

The aforesaid Component B, one-terminal-modified polyether, can be prepared by basically the same method as the production method of Component A, both-terminal-modified polyether. That is, it is prepared by an addition reaction of a polyether whose molecular chain is sealed

by group R⁴ at one terminal and with an olefin group represented by the aforesaid Formula Ia at the other terminal and a silicon hydride compound represented by the aforesaid formula Ib in the presence of the aforesaid hydrosilylation catalyst.

This Component B, one-terminal-modified polyether, is used in a proportion of from 10 to 90 % by weight, preferably from 25 to 85 % by weight, of the total amount of this component and the aforesaid Component A, both-terminal-modified polyether. If this Component B is used less than the aforesaid range, a plasticizer needs to be incorporated in a large quantity in order to obtain a cured product having a low modulus and high elongation rate. As a result, the surface of the obtained cured product exhibits oil bleeding, which leads to contamination of the cured-product surface and deterioration of the physical properties of the cured product. If it is used in a quantity that exceeds the aforesaid range, the resulting cured product tends to have unsatisfactory mechanical strength.

Component C

The curing agent used as Component C is blended in the present invention in order to bring about the condensation curing of Component A, both-terminal-modified polyether.

As this curing agent, those that are used for condensation-type silicone RTV can be used.

Concrete examples thereof include metal salts of organic acids, /362 such as dibutyltin dilaurate, dibutyltin dibenzyl maleate, dibutyltin dioctoate, iron stearate, lead octylate, tin octylate, etc.; tin compounds, such as dibutyltin oxide, dioctyltin oxide, etc.; titanitic acid esters, such as tetrabutyl titanate, tetraisopropyl titanate, etc.; titanium chelate compounds, such as titanium acetylacetonate, etc.; and mixture of these. When Component A, both-terminal-modified polyether, has an alkoxy group as the hydrolyzable group X, it is especially desirable to use a carboxylic acid salt of tin or a titanium chelate compound as the curing catalyst.

In the composition of the present invention, the aforesaid curing agent is preferably incorporated in a proportion of from 0.01 to 10 parts by weight, better yet, from 0.1 to 5 parts by weight, per total 100 parts by weight of the both-terminal-modified polyether (Component A) and one-terminal-modified polyether (Component B). If its incorporated amount is less than the aforesaid range, it does not fully exhibit its function as the curing catalyst. As a result, a longer curing time is required, and there is a tendency to cause insufficient curing deep inside the cured product. If the amount exceeds the aforesaid range, the shelf life of this composition tends to become shorter.

Other Components

The composition of the present invention may incorporate various compounding ingredients besides the aforesaid Components A through C

to an extent that does not affect the objective of the present invention. For example, it is possible to incorporate fillers, such as fumed silica, precipitated silica, hydrophobicized substances of these, silicic anhydride, hydrous silicic acid, carbon black, calcium carbonate, magnesium carbonate, diatom earth, calcined clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, zinc oxide, activated zinc oxide, hydrated castor oil, Shirasu balloon, asbestos, glass fibers, filaments, and the like, singly or in combination of two or more. It is also possible to incorporate coloring agents, such as inorganic pigments, organic dyes, etc.; adhesion-imparting agents, such as phenolic resins, epoxy resins, etc.; antioxidants; ultraviolet absorbers; and the like. In the case of obtaining cured products having an especially low hardness and large elongation, it is desirable to incorporate such fillers as titanium oxide, calcium carbonate, magnesium carbonate, talc, ferric oxide, zinc oxide, Shirasu balloon, etc., in a proportion of from 5 to 200 parts by weight per total 100 parts by weight of the aforesaid Components A and B. If the cured-product surface shows tackiness, various kinds of silanes, such as trimethoxysilane, triethoxysilane, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, etc., as well as partially hydrolyzed products of these may be incorporated as appropriate.

Curable Composition

The curable composition of the present invention can be easily formulated by mixing the aforesaid components uniformly.

This curable composition undergoes condensation curing at, for example, room temperature and forms a cured product. In the curing process, water and alcohols, such as methanol, ethanol, propanol, methyl cellosolve, etc., may be added for the purpose of accelerating the curing or improving the curing of the deep part.

The curable composition of the present invention is especially useful as a one-component type or two-component type elastic sealant, and it is suitably used as a sealing agent for buildings, marine vessels, automobiles, roads, and so forth. Furthermore, when it is used in combination with internal additives, such as aminosilane, epoxysilane, etc., or primers, it can adhere to such substrates as glass, porcelain, wood, metal, resin-formed products, and the like, and, therefore, can be used as various types of sealing compositions and adhesive compositions. In addition, it is also useful as food packaging materials, casting rubber materials, coating materials, and pad printing materials.

[Working Examples]

Working Example 1

An oxypropylene [sic] polymer having an average molecular weight of 8,000 and having the $(\text{CH}_2\text{O})_n$ $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_2\text{CH}_2\text{CH}_2\text{O} - \end{array}$ group at both terminals of the molecular chain 50 parts by weight

an oxypropylene polymer having an average molecular weight of 8,000 and having the $(\text{CH}_2\text{O})_n$ $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_2\text{CH}_2\text{CH}_2\text{O} - \end{array}$ group at one terminal of the molecular chain, the other terminal of the molecular chain being /363 sealed by a butoxy group, 50 parts by weight

calcium carbonate 140 parts by weight

titanium oxide 25 parts by weight

styrenated phenol (antioxidant) 1 part by weight

were kneaded in a condition in which substantially no moisture was present, and

dibutyltin dilaurate 1 part by weight

was subsequently added, and the ingredients were uniformly kneaded, thereby obtaining a curable composition.

From this composition, an H-type test piece was prepared according to JIS K-5758. When it was cured at 23 °C and 60 % humidity for 14 days, a rubber-like elastic product that had been cured completely to the center was obtained. When this rubber-like elastic product was subjected to a tensile test at a speed of 50 mm/minute, it

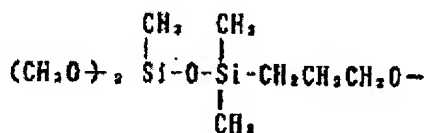
exhibited the following tensile characteristics: a 50 % modulus of 2.8 kg/cm², a rupture strength of 8.1 kg/cm², and a breaking elongation of 600 %.

In addition, from the aforesaid curable composition, a 3 mm-thick sheet-shaped sample was prepared and cured at 90 °C and 60 % humidity for 14 days, after which the surface condition was observed, and no oil bleeding was found.

Working Example 2

A curable composition was formulated from a formula that was the same as the formula used in Working Example 1, except that, in this example,

an oxypropylene polymer having an average molecular weight of



9,000 and having the

of the molecular chain

group at both terminals

60 parts by weight and

an oxypropylene polymer having an average molecular weight of 3,000 and having the same group as the above at one terminal of the molecular chain, the other terminal of the molecular chain being sealed by a butoxy group,

40 parts by weight

were used in place of the oxypropylene polymers used in Working Example 1.

The tensile characteristics of an H-type test piece that was prepared from this curable composition in the same manner as in

Working Example 1 exhibited the following tensile characteristics after it was cured at 23 °C and 60 % humidity for 14 days: a 50 % modulus of 2.5 kg/cm², a rupture strength of 6.5 kg/cm², and a breaking elongation of 550 %. In addition, the same sheet-shaped sample as the one in Working Example 1 was prepared and observed under the same conditions, and no oil bleeding was found.

Working Example 3

A curable composition was formulated from a formula that was the same as the formula used in Working Example 1, except that, in this example,

an oxypropylene polymer having an average molecular weight of 8,400 and having the $(CH_2O)_x - \overset{\overset{CH_3}{|}}{Si} - CH_2CH_2CH_2 - NHCO-O -$ group at both terminals of the molecular chain 50 parts by weight and

an oxypropylene polymer having an average molecular weight of 8,400 and having the $(CH_2O)_x - \overset{\overset{CH_3}{|}}{Si} - CH_2CH_2CH_2 - NHCO-O -$ group at one terminal of the molecular chain, the other terminal of the molecular chain being sealed by a butoxy group, 50 parts by weight were used in place of the oxypropylene polymers used in Working Example 1.

The tensile characteristics of an H-type test piece that was prepared from this curable composition in the same manner as in Working Example 1 showed the following tensile characteristics after

it was cured at 23 °C and 60 % humidity for 14 days: a 50 % modulus of 2.5 kg/cm², a rupture strength of 8.0 kg/cm², and a breaking elongation of 650 %. In addition, the same sheet-shaped sample as the one in Working Example 1 was prepared and observed under the same conditions, and no oil bleeding was found.

[Effects of the Invention]

According to the present invention, it was possible to obtain curable compositions from which cured products that showed no oil bleeding at all and that had a low modulus and high elongation rate could be formed.